

# PATENT ABSTRACTS OF JAPAN

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## **(54) HYDROGENATION CRACKING CATALYST FOR MEDIUM DUTY DISTILLED OIL PRODUCTION**

### **(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a catalyst which can be used for producing a variety of diesel oil with advantages such as outstanding hydrogenation cracking properties and hydrogenation dewaxing properties, the high quality of obtained hydro genation cracked finished products, and the wide distillation range of a diesel fraction which can be used for the production of especially, the diesel oil at a low freezing temperature.

**SOLUTION:** This hydrogenation cracking catalyst has the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 30-90, the acidity of 0.1-0.5 mmol/g and the moisture adsorption power of 10 wt.% or less when a temperature is 25°C and a steam pressure is 12 mmHg or less. In addition, the catalyst is composed of 5-40 wt.% of modified superhydrophobic zeolite- $\beta$ , 10-50 wt.% of amorphous silica-alumina, 15-30 wt.% of alumina, 10-40 wt.% of at least, one of group VIb metallic oxide and 1-10 wt.% of at least, one of group VIII metallic oxide.

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**CLAIMS**

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[Claim(s)]

[Claim 1] As an acidic component, an amorphous silica alumina is included and it is the denaturation super-hydrophobic-property zeolite of the degree of bottom-acid nature. - beta, It consists of a VIII group metal. the [ in the type of a metallic oxide as a hydrogenation component / at least one periodic-table / which is supported ] -- the / VIb group metal and / at least one / which is supported / - The inclusion proportion of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> in the aforementioned zeolite-beta is 30-90. The hydrocracking catalyst for producing a nature distillate while water adsorbability in case the acidity measured by the pyridine adsorption IR method is [ a water vapor pressure ] 12 or less mmHg at 0.1-0.5mmol/g and the temperature of 25 degrees C is 10% or less.

[Claim 2] 5 - 40wt% of the aforementioned denaturation -- super- -- the [ hydrophobic zeolite-beta, amorphous 10 - 50wt% silica-alumina, 15, - 30wt% alumina, 10, - 40wt% / at least one ] -- the [ VIb group metallic-oxide and at least one 1 - 10wt% ] -- the catalyst according to claim 1 characterized by consisting of a VIII group metallic oxide

[Claim 3] The catalyst according to claim 1 characterized by the acidity which the specific surface area of a catalyst measured by 200-300m<sup>2</sup>/g, and pore volume measured by 0.3-0.4ml [ g ]/and the pyridine adsorption IR method being 0.3-0.5mmol/g.

[Claim 4] When the aforementioned denaturation super-hydrophobic-property zeolite-beta carries out hydrothermal processing after the step of the deamination by the mosquito glow, and dealminizationizing by acid treatment, and under the hyperbaric pressure, it is H- type zeolite. - Catalyst according to claim 1 characterized by being prepared from beta.

[Claim 5] It is the catalyst according to claim 4 to which the aforementioned hydrothermal processing is characterized by carrying out preferably for 0.5 to 5 hours at the temperature of 400-900 degrees C under the vapor pressure of 50-500KPa for at least 0.5 hours.

[Claim 6] the [ aforementioned ] -- the catalyst according to claim 2 to which VIb group metal is chosen from Mo and/or W, and the content is characterized by being 10 - 40wt% on all the weight criteria of a catalyst in the type of a metallic oxide

[Claim 7] the [ aforementioned ] -- VIII group metal -- Co and/-- the catalyst according to claim 2 to which it is again chosen from nickel and the content is characterized by being 1 - 10wt% on all the weight criteria of a catalyst in the type of a metallic oxide

[Claim 8] 10 - 30wt% of denaturation -- super- -- the [ hydrophobic zeolite-beta, amorphous 20 - 40wt% silica-alumina, 15, - 30wt% alumina, 20, - 30wt% ] -- the [ VIb group metallic-oxide, 4, - 8wt% ] -- the catalyst according to claim 2 which consists of a VIII group metallic oxide

[Claim 9] The catalyst according to claim 2 characterized by the acidity which specific surface area measured by 300-500m<sup>2</sup>/g ten to 60%, and pore volume measured [ SiO<sub>2</sub> content of the aforementioned amorphous silica alumina ] by 0.7-1.2ml [ g ]/and the pyridine adsorption IR method being 0.3-0.5mmol/g.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the hydrocracking catalyst for a hydrocracking catalyst, especially the nature distillate production of inside.

[0002]

[Description of the Prior Art] Now, in the refinery in the world, it is observed as one of the most important meanses for the raw material which refines oil having made it heavy, and being faced with the problem that a quality also deteriorates, so a hydrocracking process \*\*\*\*\*ing heavy oil. The need over the nature distillate of the inside in the world is increasing continuously, there are a hydrogenation catalyst for the nature distillate production of inside and a function to make the nature distillates of inside, such as a navigation-light oil and Diesel oil, produce to the upper limit of the capacity rating especially, in connection with it, and, moreover, the development of the hydrocracking catalyst with the flexibility about operation use is activating.

[0003] A hydrocracking catalyst is a dual function catalyst which has both hydrogenation and a cracking function. the case of the hydrocracking catalyst of the conventional non-noble-metals system -- the [ periodic-table ] -- the [ VIb group and ] -- generally VIII group metal is used as a hydrogenation component, and the crystal zeolite and/or the amorphous silica alumina are chosen as an acidic component Although it has high selectivity in itself when an amorphous silica alumina is used independently, the catalytic activity is low and its versatility on use is also low. Then, it can be used by introducing a new zeolite material combining these two materials, and the hydrogenation catalyst of a new mold which has the high catalytic activity to a middle distillate and selectivity can be obtained.

[0004] the zeolite of a pore size with the crystalline large zeolite for a hydrogenation catalyst in the conventional technique, for example, zeolite-X, and -Y -- it consists of zeolite-Y preferably A macromolecule hydrocarbon will enter into the pore of the zeolite converted there with this catalyst. In the case of the raw material of the paraffin base, the Diesel oil with which cracking of the fraction 343 degrees C or more is carried out to the fraction which is 165-343 degrees C, and it is obtained has a high freezing point, therefore the yield of the nature distillate of inside also falls. As a cracking catalyst of another mold, although there are some which used the parvus zeolite or shape-selectivity zeolite of a pore size like ZSM-5 as a cracking component, only the alkane with a straight chain or a short side chain can go into the pore structure of a zeolite, for example, the hydrocarbons of a straight chain will be converted, and a \*\* low will be carried out, therefore the freezing point becomes low from Diesel oil and tail oil. In this zeolite, pore will not be removed at a parvus sake, and a reactant will not be removed by within a time, but superfluous cracking will happen as the result, and the selectivity to a middle distillate will fall. Furthermore, the hydrocarbon of the amount of macromolecules cannot go into pore. When treating a heavy raw material especially, catalytic activity will fall.

[0005] It is indicated about #3812 catalyst by the "China refinery technique" (Hou Xiang-lin Mr.

editorial supervision, pp.511, SINOPEC press). This catalyst processes heavy stock oil, and by performing hydrocracking and a \*\*\*\*\* low simultaneously, when producing the nature distillate of the inside of a premium, low freezing-point Diesel oil, and lubricous base oil, it is used. The characteristic feature of this catalyst is using zeolite-beta. Although the quality of the hydrocracking production acquired using this catalyst is good, when using this catalyst for processing of heavy stock oil, generally 390 degrees C or more are required for reaction temperature. For example, if Daqing VGO is processed, although light oils, such as naphtha, are producible with the reaction temperature of 393 degrees C, 70wt%, an one step invert ratio is 27.9wt%, and the selectivity to a middle distillate has [ the yield of gas and a gasoline ] it. [ low ]

[0006] The hydrocracking process is indicated by U.S. JP,4,B and 820,402. Here, the improved selectivity in a production of the distillate product in the domain of 165-343 degrees C is obtained by using the zeolite with the inclusion proportion of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> high as an acidic component. in order to make the selectivity to a middle distillate increase and to cut down hydrogen consumption in this patent -- the mole ratio of the silica/alumina of the zeolite component in a catalyst -- at least 50:1 -- it is indicated that it is desirable and it is required 100:1 and to be 200:1 more preferably If it is used under the condition by which the invert ratio was controlled to 60v% in the catalyst indicated by this patent when processing Arabian VGO, the selectivity to a middle distillate will serve as 45 - 65v%.

[0007] In another zeolite of the high inclusion ratio (SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub>= 200:1) of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> used for a catalyst, the selectivity which is different to a middle distillate is shown, and the sequence serves as ZSM-20> zeolite-beta> zeolite-Y from the higher one. The best thing is a catalyst containing ZSM-20 and the space velocity of the selectivity is 72v% to a middle distillate under the condition of 0.54hr<sup>-1</sup>. Zeolite-beta is used as an acidic component, and when an invert ratio is 60v%, the selectivity to a middle distillate is less than [ 70v% ].

[0008] Although the selectivity to a middle distillate is 86v% when the hydrocracking catalyst which consists of zeolite-Y UHP-Y is stated to EP0028938 and Arabian VGO is processed using this catalyst, the invert ratio is 60v% slightly. In processing Kuwait VGO with easy cracking, reaction temperature turns into high temperature called 407 degrees C. If this reaction temperature is lowered to 397 degrees C, the selectivity to a middle distillate will become 74v% only.

[0009]

[Problem(s) to be Solved by the Invention] The purpose of this invention is offering the middle-distillate hydrocracking catalyst which processes a heavy hydrocarbon raw material and can be used for a production of the nature distillate of inside. Still another purpose of this invention is a zeolite as a main acidic component which has the capacity to be high catalytic activity, the high selectivity to a middle distillate, the versatility on use, and a capacity rating to an upper limit, and to make the high navigation-light oil of the smoke point, and the Diesel oil which has a large \*\*\*\* domain and a low freezing point produce. - It is offering the middle-distillate hydrocracking catalyst which consists of beta.

[0010]

[Means for Solving the Problem] the catalyst of this invention -- the acidic component of denaturation zeolite-beta as a main acidic component, and an addition, the amorphous silica alumina as a carrier, and a hydrogenation component \*\*\*\*\* -- the [ periodic-table ] -- the [ at least one metal which is chosen from VIb group and which is supported, and ] -- it consists of at least one metal which is chosen from VIII group and which is supported The acidity (following, acidity) which measured the specific surface area of the catalyst of this invention by 200-300m<sup>2</sup>/g, and measured pore volume by 0.3-0.4ml [ g ]/and the pyridine adsorption IR method is 0.3-0.5mmol/g. As for the acidity of denaturation zeolite-beta of the catalyst concerning this invention, 30-90, and the Na<sub>2</sub>O content of 0.1-0.5mmol/g and the inclusion proportion (chemistry method) of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> are <0.2wt%.

[0011] the catalyst concerning this invention -- the [ denaturation zeolite-a 5 - 40wt% beta, non-fixed

form a 10 - 50wt% silica-alumina, 15 - 30wt% (it calculates as xeransis alumina) binder, 10, - 40wt% ] -- the [ VIb group metal (preferably Mo and/or W), 1, - 10wt% (it calculates as a metallic oxide) ] -- it consists of a VIII group metal (preferably Co and/or nickel)

[0012] With the conventional technique, this zeolite-beta is passing through the two following steps, makes the inclusion proportion of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> increase, and becomes possible

[ denaturalizing ]. 1. Step which carries out mosquito glow of several hours zeolite-beta at 500-600 degrees C in order to remove deamination:organic amine mold (template agent) by mosquito glow in elevated temperature. 2. Step which inorganic acid of a certain concentration and zeolite-beta are made to react, and removes aluminum from skeleton of zeolite-beta at specific temperature in order to make inclusion proportion of dealminization-ized:SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> by acid treatment increase.

[0013] After it reduces the acidity of zeolite-beta of a start material to 0.8-1.0mmol/g after making it deaminate by the mosquito glow in an elevated temperature, and processing of an acid performs dealminization-ization after that, the acidity of zeolite-beta is reduced to 0.5-0.6mmol/g. It is not enough for making the selectivity to a middle distillate increase substantially although the amount of the solid acid of the above-mentioned denaturation zeolite-beta can be reduced to some extent.

[0014]

[Embodiments of the Invention] It prepares by carrying out acid treatment of the zeolite-beta for carrying out a mosquito glow of the zeolite-beta of a start material for denaturation zeolite-beta of this invention for deamination, and dealminization-izing, and carrying out hydrothermal processing under the hyperbaric pressure after that. The inclusion proportion of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> of denaturation zeolite-beta concerning this invention can be high, the amount of a solid acid can be reduced, and denaturation zeolite-beta used with the hydrocracking catalyst which starts this invention by doing so can provide a catalyst now with the outstanding selectivity to a middle distillate.

[0015] Zeolite-beta used with the catalyst concerning this invention is the denaturation zeolite prepared according to the process of the above-mentioned this invention. - Since it is beta, and this gives the high adsorptivity to a non-polar hydrocarbon and only a low adsorptivity is shown in a polar molecule like water, it is usually a hydrophobic zeolite. - It is referred to as beta or denaturation super-hydrophobic-property zeolite-beta. The diameter of the pore of the above-mentioned zeolite-beta used with the catalyst concerning this invention is >5x10-10m. Hydrothermal processing is 400-900 degrees C in temperature after the deamination by the mosquito glow, and dealminization-izing by acid treatment, and under the water vapor pressure of 50-500KPa, and the process feature which prepares the above-mentioned zeolite-beta is a thing made preferably in 0.5 - 5 hours for 0.5 hours of being few.

[0016] Although it is changing the structure of a zeolite in order for the purpose of hydrothermal processing of zeolite-beta currently used by this invention to make the selectivity of the hydrocracking catalyst over a middle distillate increase, hydrothermal processing before dealminization-izing by a mosquito glow or acid treatment under an elevated temperature in the conventional technique of the technique (the purpose of this processing is mainly removing organic amine mold from a zeolite) is another.

[0017] After dealminization-izing, the amount of the acid fraction of zeolite-beta concerning this invention decreases, and the acidity also falls to 0.2-0.3mmol/g preferably 0.1 to 0.5 mmol/g. For this reason, although the requirements in the hydrocracking catalyst cracking activity of this invention for producing the nature fraction of inside are fulfilled, since there is a site with low acidity on the other hand, the possibility of the 2nd cracking decreases. In another side, the grade of dealminization-izing of zeolite-beta of this invention is controlled severely, and the inclusion ratio of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> in denaturation zeolite-beta obtained here serves as the domain of 30-90.

[0018] Denaturation super-hydrophobic-property zeolite-beta of this invention is a denaturation zeolite which has the degree of bottom-acid nature. It is the denaturation zeolite which has sufficient

cracking activity as compared with zeolite-Y although the acidity of denaturation zeolite-beta of this invention is low, therefore is combined with an acid amorphous silica alumina, and becomes one component as shown in Table 1. - The hydrocracking catalyst of this invention which consists of beta shows not only high acidity but the high selectivity to a middle distillate. Furthermore, since comparatively high structure destructive temperature is held, this catalyst is excellent in the thermal stability. Thus, it can use not only the outstanding selectivity [ as opposed to good catalytic activity or a good middle distillate for the above-mentioned zeolite-beta concerning this invention ] but in order to prepare the hydrocracking catalyst which shows a good thermal stability and the resistance over a nitrogen poisoning or a carbon store.

[0019]

[Table 1] (Table 1: Property of zeolite-beta before and behind denaturation)

ゼオライトの型	USY	Hゼオライト- $\beta$	本発明のゼオライト- $\beta$
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>			
の比率(mol/mol)	6.55	49.16	62.16
酸性度(mmol/g)			
B 酸性	0.634	0.245	0.115
L 酸性	0.301	0.184	0.097
B+L 酸性	0.935	0.429	0.212
構造破壊温度(℃)	1080	1340	1420

An amorphous silica alumina is used for the catalyst concerning this invention as the acidic component and carrier component of an addition of a catalyst. 10 - 60wt%, as for specific surface area, 0.7-1.2ml [ g ] /and acidity are 0.3-0.5mmol/g, an activity carrier component and a zeolite component give cracking activity to union \*\*\*\*\* and a catalyst, and 300-500m<sup>2</sup>/g and pore volume support [ the content of SiO<sub>2</sub> in this amorphous silica alumina ] the metal component for hydrogenation.

[0020] By the conventional various techniques known well, a pellet product and in order to extrude, to be made to a configuration like a product and to support a metal, the technique of the catalyst concerning this invention, such as coprecipitation, kneading, mixture, and sinking in, is also usable. As for the metal component of the catalyst product concerning this invention, preparing by technique, such as extrusion molding and sinking in, is desirable. Especially the catalyst of this invention, adding the 15 - 30wt% (catalyst all weight criteria) binder prepared by carrying out the peptization of the small pore alumina from an acid like a nitric acid This invention [ 5 - 40wt% of ] (catalyst all weight criteria) denaturation zeolite-beta is mixed to 30 - 80wt% (catalyst all weight criteria) the xeransis powder and homogeneity of an amorphous silica alumina. The mixture is kneaded with a paste. then, generally Extrusion molding is carried out to the bar of the cartridge whose diameter is 1.3-1.8mm, or a special configuration product like a crowbar form. furthermore, after that, a carrier is dried and it activates by the mosquito glow -- making -- the [ at least one periodic-table ] -- the [ VIb group metal and / at least one ] -- the solution containing the hydrogenation metals supported, such as VIII group metal It is prepared from activating in order to make it sink in by the pore saturation or the solution sinking-in method, to dry further the carrier rod with which those metals are supported after that and to acquire the catalyst of this invention.

[0021] The catalyst of this invention is a 10 - 30wt% denaturation zeolite on the basis of the total weight of a catalyst. - beta, A 20 - 40wt% (it calculates as a xeransis alumina) amorphous silica alumina, the [ periodic-table ] -- the [ a 20 chosen from VIb group, - 30wt% (it calculates as a metallic oxide) metal (preferably Mo and/or W), and ] -- a 4 chosen from VIII group, - 8wt% (it calculates as a metallic oxide) metal (preferably) It is desirable that Co and/or nickel are included.

[0022] Although the catalyst of this invention used for hydrocracking is suitable when processing the heavy hydrocarbon raw material which has 250-600 degrees C in the \*\*\* domain of 300-550 degrees C especially preferably, it has gas oil, a vacuum distillate, a deasphalted oil, the recycling oil generated from catalyst cracking, \*\*\*\*, a coal tar, etc. as stock oil which has the special feature described above. Generally, for 100-5000, and space velocity to happen by 0.1-5.0hr-1, and, as for this reaction, reaction temperature is made for the proportion of 5 - 20MPa, hydrogen, and oil to happen [ the bottom of hydrogen presence, and reaction pressure ] at 350-450 degrees C. A hydrocracking process consists of a prior processing phase of the hydrorefining for saturating the polycyclic formula aromatics in stock oil so that relief of the severe operation status in the case of performing the phase and hydrocracking which remove most of S and N from stock oil can be performed. The catalyst of this invention can show comparatively strong resistance to nitrogen, that is, for the reason, a catalyst can be independently used by realizing versatility on use by that cause, and a heavy hydrocarbon raw material can be processed in a single-stage process using a single catalyst. This catalyst shows high selectivity to comparatively high catalytic activity and middle distillate.

[0023] In case the catalyst concerning this invention is used for processing of usual VGO, the bottom of presence of hydrogen and a pressure are [ the reaction ] desirable, and reaction temperature is [ for 500-2000, and space velocity to happen by 0.5-2.0hr-1, and ] made for the proportion of 10 - 20MPa and hydrogen pair oil to happen at 370-420 degrees C. According to hydrocracking, in case the catalyst concerning this invention produces the nature distillate of inside, it has high catalytic activity and the selectivity to a middle distillate. # When it is the same technique as the case of #3812, i.e., the almost same invert ratio, about the catalyst of this invention, reaction temperature is made into 389 degrees C and Daqing VGO is processed for the comparison with 3812 hydrocracking catalyst, the selectivity to a middle distillate is 75w%. It is possible to produce the kerosene for aeronautical navigation and Diesel oil to a production upper limit by being able to use it for operation with the full recycling mode or the single path mode which the versatility on operation use is in the catalyst of this invention, for example, was doubled with the requirements on a product, and regulating an operating condition. Furthermore, the catalyst of this invention shows the performance which was excellent in hydrocracking and the point of a \*\*\*\*\* low, and the quality of the product which was obtained according to hydrocracking for the reason is excellent. The Diesel oil of a low freezing point can be produced by using the catalyst of this invention especially, the domain of the \*\*\* boundary point of a diesel fraction is wide, and this is convenient to production increase of Diesel oil.

[0024]

[Example] this invention is explained still in detail with reference to the following example. Instantiation is the purpose and, as for the example explained here, this invention is not limited to these examples.

[0025] [Example 1] H type zeolite-beta ( $\text{SiO}_2 / \text{aluminum}_2\text{O}_3 = 25.1$ ) was processed by 0.5N and HCl for 2 hours, and it carried out hydrothermal processing at 750 degrees C for 2 hours so that water adsorbability in case water vapor pressures are 12mmHgs at 25 degrees C might become 2.6wt% further so that water adsorbability in case the inclusion proportion of  $\text{SiO}_2 / \text{aluminum}_2\text{O}_3$  is [ water vapor pressures ] 12mmHgs at 48 or 25 degrees C might become 16.9wt%. Zeolite of after xeransis and this invention - beta (FA) was obtained. adding the binder (binder) prepared by carrying out the peptization of the pseudo-boehmite which has 28g small pore in the catalyst (CA) of this invention using the dilution nitric-acid solution made to melt 5.7ml of a nitric acid in 85ml distilled water 40% 20.7g zeolite FA, the amorphous silica alumina (the content of  $\text{SiO}_2 = 45\text{wt\%}$ ) with 86.3g big pore 0.956ml [ g ] /and acidity 0.40mmol/g, [ specific surface area ] [ 365m<sup>2</sup>/g and pore volume ] 47g meta-tongue state ammonium and 42.1g nickel nitrate are mixed uniformly. Knead to a paste the mixed liquor obtained as a result, and a diameter extrudes it through the plate with a hole with 1.7mm cylinder-like pore further. After [ which extruded and dried the rod at 110 degrees C for 3 hours ] obtaining as a result, by making it activate at 500 degrees C A 23.8wt%  $\text{WO}_3$ , a 7.4wt%  $\text{NiO}$ , 10wt%

hydrophobic zeolite - It consisted of beta and catalyst CA whose pore volume specific surface area is 264m<sup>2</sup>/g, and is 0.322ml/g was obtained.

[0026] [Example 2] H type zeolite-beta (SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub>= 25.1) so that water adsorbability in case the inclusion proportion of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> is [ water vapor pressures ] 12mmHgs at 48 or 25 degrees C may become 16.9wt% It processes by 0.5N and HCl for 2 hours, hydrothermal processing is carried out at 550 degrees C for 2 hours, and it dries after that so that water adsorbability in case water vapor pressures are 12mmHgs at 25 degrees C may become 7.3wt% further, and it is the zeolite of this invention. - beta (FB) was obtained. the amorphous silica alumina (the content of SiO<sub>2</sub> -- 25wt% --) with the big pore (41.6g and 116.4g) of the zeolite FB 332m<sup>2</sup>/g and pore volume are mixed in 0.922ml [ g ], and acidity mixes [ specific surface area ] 0.34mmol/g uniformly. Then, the binder which was made to carry out the peptization of the pseudo-boehmite with 28g small pore, and prepared it with the dilution nitric-acid solution made to melt 5.7ml 40% nitric acid in 85ml distilled water is added. Furthermore, after that, make mixed liquor knead with a paste and it is extruded through the plate with a hole with the pore of the shape of a cylinder whose diameter is 1.7mm. Dry the extruded rod at 110 degrees C, it was made to activate at 500 degrees C for 3 hours, a 39g molybdenum oxide, 41g nickel nitrate, and the solution prepared from 85% of H<sub>3</sub>PO<sub>4</sub> were infiltrated, and the carrier was produced. The carrier with which a metal is supported is activated at 500 degrees C after that for 3 hours, and it is a 23.4wt% MO<sub>3</sub>, 6.7wt% NiO, and 15wt% hydrophobic zeolite. - It consisted of beta and the catalyst (CB) of this invention whose pore volume specific surface area is 268m<sup>2</sup>/g, and is 0.329ml/g was acquired.

[0027] the amorphous silica alumina (the content of SiO<sub>2</sub> -- 35wt% --) of the large pore (62.4g and 106.3g) of zeolite FA obtained in the [example 3] example 1 396m<sup>2</sup>/g and pore volume are mixed in 0.996ml [ g ], and acidity mixes [ specific surface area ] 0.34mmol/g uniformly. The binder prepared by carrying out a peptization with the dilution nitric-acid solution which melted 5.7ml of a nitric acid in 85ml distilled water 40% is added. Make the mixed liquor obtained as a result knead with a paste, and it extrudes after that through the hole vacancy plate with the cylinder-like pore whose diameter is 1.7mm. Extrude, dry a rod at 110 degrees C, and the carrier into which the solution which was obtained as a result, and which was prepared by 47g meta-tongue state ammonia and 42.1g nickel nitrate was infiltrated is obtained. Furthermore, it is made to activate at 500 degrees C for 3 hours, and is a 24.5wt% WO<sub>3</sub>, 6.8wt% NiO, and 30wt% hydrophobic zeolite. - It consisted of beta and the catalyst (CC) of this invention whose pore volume specific surface area is 278m<sup>2</sup>/g, and is 0.318ml/g was acquired.

[0028] It prepared by the same technique as an example 1 except having used zeolite Y (acidity being 1.1mmol/g) of a super-hydrophobic property, such as USY which described above the [example 1 of example 4= comparison] contrast catalyst instead of hydrophobic zeolite-beta in this invention. This contrast catalyst consisted of a 22.3wt% MoO<sub>3</sub>, a 7.2wt% NiO, and 15wt% zeolite Y, and the specific surface area is 301m<sup>2</sup>/g, pore volume is 0.386ml/g, and it considered as the contrast catalyst (YC).

[0029] 14.7MPas and hydrogen pair oil proportion used 1200, the pressure used 200ml fixed-bed reactor on condition that 1.5hr-1, and space velocity evaluated the catalyst in the [example 5] examples 1-4. The catalyst was made to sulfurate before evaluation. Table 2 shows the property of the evaluated raw material oil. In the case of the one step in-series process, the 2nd reactor was filled up with the hydrocracking catalyst and the 1st reactor was filled up with the hydrorefining catalyst. Consequently, the nitrogen content of the refining oil included in the 2nd reactor became [g] less than in 10microg /. Table 3 shows the evaluation result of an one step in-series process. Table 4 shows the evaluation result of the one step in-series process of full recycling operation, and shows the property of the processing product in Table 5. Because of the strong resistance over the acidic-site property and nitrogen, the catalyst of this invention is the single-stage process which used the single catalyst, and can process a raw material. Table 6 is as a result of [ at the time of processing Daqing VGO according to the single-stage process which used a single catalyst and contrast catalyst #3812 ]

evaluation.

[0030]

[Table 2] (Table 2: Property of raw material oil)

原料オイル	Shengli VGO	Daqing VGO	Saudi Arabian VGO
密度(g/cm <sup>3</sup> )	0.8861	0.8571	0.9133
留出範囲(℃)			
IBP	294	284	319
50%	443	453	432
95%	529	531	504
残留炭素(wt%)	0.15	0.04	0.08
S (wt%)	0.53	0.07	2.20
N (wt%)	1.72	0.54	0.79

[0031]

[Table 3] (Evaluation result of 3:1 steps of tables in-series process uniproCESSING) <IMG -- solvent-refined-coal="/NSAPITMP2/web176/IMAGE/20010809023251885115.gif" -- WIDTH="--432" HEIGHT="--294" ALT=" ID=000004" -->

[0032]

[Table 4] (Evaluation result of 4:1 steps of tables in-series process full recycling processing)

N.o.	1004	1005
触媒	C B	Y C
原料	Shengli VGO	Shengli VGO
反応温度(℃)	380	384
製品内訳(原料基準vol%)		
ライトナフサ	12.8	23.2
ヘビーナフサ	14.9	16.1
航空用灯油	47.1	44.6
ディーゼル油	33.2	24.0
C <sub>6</sub> ・液状物収率	108.0	107.9

[0033]

[Table 5] (Table 5: Property of a hydrocracking product)

N.o.	1001	1002	1003	1004	1005
航空用灯油の発煙点	26	27	28	30	28
ディーゼル油の凍結温度	-11	-14	-17	-12	0

[0034]

[Table 6] (Table 6: It evaluates as a result of a single catalyst and one step process processing)

触媒	#3812	C B
原料	Daqing VGO	Daqing VGO
容積空間速度( $hr^{-1}$ )	1.0	1.0
反応温度(℃)	393	389
製品内訳(原料vol%)		
ガソリン	24.7	17.2
灯油	31.1	32.7
ディーゼル	11.2	17.7
テール油	29.8	30.9
液状物収率	96.8	98.5
中質油選択率(%)	63.1	74.6

\* The source of the data of notes:catalyst #3812 is "China refining technique". Although pp.511 this invention is explained in detail by the example, it is understood by this contractor in the pneuma of this invention that corrections and enhancements various to deviation \*\*\*\* are possible. Therefore, it is clear that all of these corrections and enhancements are within the limits of this invention.  
[0035]

[Effect of the Invention] The catalyst of this invention can produce a navigation-light oil and Diesel oil to a production upper limit by there being versatility on operation use and regulating an operating condition. Furthermore, the catalyst of this invention shows the performance which was excellent in hydrocracking and the point of a \*\*\*\*\* low, and the product of the quality which was excellent with hydrocracking for the reason is obtained. The Diesel oil of a low freezing point is especially producible, and the domain of the \*\*\*\* boundary point of a diesel fraction is wide, and is suitable for production increase of Diesel oil.

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[Translation done.]

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Field

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[The technical field to which invention belongs] this invention relates to the hydrocracking catalyst for a hydrocracking catalyst, especially the nature distillate production of inside.

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Technique

[Description of the Prior Art] Now, in the refinery in the world, it is observed as one of the most important meanses for the raw material which refines oil having made it heavy, and being faced with the problem that a quality also deteriorates, so a hydrocracking process \*\*\*\*\*ing heavy oil. The need over the nature distillate of the inside in the world is increasing continuously, there are a hydrogenation catalyst for the nature distillate production of inside and a function to make the nature distillates of inside, such as a navigation-light oil and Diesel oil, produce to the upper limit of the capacity rating especially, in connection with it, and, moreover, the development of the hydrocracking catalyst with the flexibility about operation use is activating.

[0003] A hydrocracking catalyst is a dual function catalyst which has both hydrogenation and a cracking function. the case of the hydrocracking catalyst of the conventional non-noble-metals system -- the [ periodic-table ] -- the [ VIb group and ] -- generally VIII group metal is used as a hydrogenation component, and the crystal zeolite and/or the amorphous silica alumina are chosen as an acidic component Although it has high selectivity in itself when an amorphous silica alumina is used independently, the catalytic activity is low and its versatility on use is also low. Then, it can be used by introducing a new zeolite material combining these two materials, and the hydrogenation catalyst of a new mold which has the high catalytic activity to a middle distillate and selectivity can be obtained.

[0004] the zeolite of a pore size with the crystalline large zeolite for a hydrogenation catalyst in the conventional technique, for example, zeolite-X, and -Y -- it consists of zeolite-Y preferably A macromolecule hydrocarbon will enter into the pore of the zeolite converted there with this catalyst. In the case of the raw material of the paraffin base, the Diesel oil with which cracking of the fraction 343 degrees C or more is carried out to the fraction which is 165-343 degrees C, and it is obtained has a high freezing point, therefore the yield of the nature distillate of inside also falls. As a cracking catalyst of another mold, although there are some which used the parvus zeolite or shape-selectivity zeolite of a pore size like ZSM-5 as a cracking component, only the alkane with a straight chain or a short side chain can go into the pore structure of a zeolite, for example, the hydrocarbons of a straight chain will be converted, and a \*\* low will be carried out, therefore the freezing point becomes low from Diesel oil and tail oil. In this zeolite, pore will not be removed at a parvus sake, and a reactant will not be removed by within a time, but superfluous cracking will happen as the result, and the selectivity to a middle distillate will fall. Furthermore, the hydrocarbon of the amount of macromolecules cannot go into pore. When treating a heavy raw material especially, catalytic activity will fall.

[0005] It is indicated about #3812 catalyst by the "China refinery technique" (Hou Xiang-lin Mr. editorial supervision, pp.511, SINOPEC press). This catalyst processes heavy stock oil, and by performing hydrocracking and a \*\*\*\*\* low simultaneously, when producing the nature distillate of the inside of a premium, low freezing-point Diesel oil, and lubricous base oil, it is used. The characteristic feature of this catalyst is using zeolite-beta. Although the quality of the hydrocracking production acquired using this catalyst is good, when using this catalyst for processing of heavy stock

oil, generally 390 degrees C or more are required for reaction temperature. For example, if Daqing VGO is processed, although light oils, such as naphtha, are producible with the reaction temperature of 393 degrees C, 70wt%, an one step invert ratio is 27.9wt%, and the selectivity to a middle distillate has [ the yield of gas and a gasoline ] it. [ low ]

[0006] The hydrocracking process is indicated by U.S. JP,4,B and 820,402. Here, the improved selectivity in a production of the distillate product in the domain of 165-343 degrees C is obtained by using the zeolite with the inclusion proportion of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> high as an acidic component. in order to make the selectivity to a middle distillate increase and to cut down hydrogen consumption in this patent -- the mole ratio of the silica/alumina of the zeolite component in a catalyst -- at least 50:1 -- it is indicated that it is desirable and it is required 100:1 and to be 200:1 more preferably If it is used under the condition by which the invert ratio was controlled to 60v% in the catalyst indicated by this patent when processing Arabian VGO, the selectivity to a middle distillate will serve as 45 - 65v%.

[0007] In another zeolite of the high inclusion ratio (SiO<sub>2</sub> / aluminum<sub>2</sub>O = 200:1) of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> used for a catalyst, the selectivity which is different to a middle distillate is shown, and the sequence serves as ZSM-20> zeolite-beta> zeolite-Y from the higher one. The best thing is a catalyst containing ZSM-20 and the space velocity of the selectivity is 72v% to a middle distillate under the condition of 0.54hr<sup>-1</sup>. Zeolite-beta is used as an acidic component, and when an invert ratio is 60v%, the selectivity to a middle distillate is less than [ 70v% ].

[0008] Although the selectivity to a middle distillate is 86v% when the hydrocracking catalyst which consists of zeolite-Y UHP-Y is stated to EP0028938 and Arabian VGO is processed using this catalyst, the invert ratio is 60v% slightly. In processing Kuwait VGO with easy cracking, reaction temperature turns into high temperature called 407 degrees C. If this reaction temperature is lowered to 397 degrees C, the selectivity to a middle distillate will become 74v% only.

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[Translation done.]

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**Effect**

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[Effect of the Invention] The catalyst of this invention can produce a navigation-light oil and Diesel oil to a production upper limit by there being versatility on operation use and regulating an operating condition. Furthermore, the catalyst of this invention shows the performance which was excellent in hydrocracking and the point of a \*\*\*\*\* low, and the product of the quality which was excellent with hydrocracking for the reason is obtained. The Diesel oil of a low freezing point is especially producible, and the domain of the \*\*\* boundary point of a diesel fraction is wide, and is suitable for production increase of Diesel oil.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] The purpose of this invention is offering the middle-distillate hydrocracking catalyst which processes a heavy hydrocarbon raw material and can be used for a production of the nature distillate of inside. Still another purpose of this invention is a zeolite as a main acidic component which has the capacity to be high catalytic activity, the high selectivity to a middle distillate, the versatility on use, and a capacity rating to an upper limit, and to make the high navigation-light oil of the smoke point, and the Diesel oil which has a large \*\*\*\* domain and a low freezing point produce. - It is offering the middle-distillate hydrocracking catalyst which consists of beta.

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**MEANS**

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[Means for Solving the Problem] the catalyst of this invention -- the acidic component of denaturation zeolite-beta as a main acidic component, and an addition, the amorphous silica alumina as a carrier, and a hydrogenation component \*\*\*\*\* -- the [ periodic-table ] -- the [ at least one metal which is chosen from VIb group and which is supported, and ] -- it consists of at least one metal which is chosen from VIII group and which is supported The acidity (following, acidity) which measured the specific surface area of the catalyst of this invention by 200-300m<sup>2</sup>/g, and measured pore volume by 0.3-0.4ml [ g ] /and the pyridine adsorption IR method is 0.3-0.5mmol/g. As for the acidity of denaturation zeolite-beta of the catalyst concerning this invention, 30-90, and the Na<sub>2</sub>O content of 0.1-0.5mmol/g and the inclusion proportion (chemistry method) of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> are <0.2wt%.

[0011] the catalyst concerning this invention -- the [ denaturation zeolite-a 5 - 40wt% beta, non-fixed form a 10 - 50wt% silica-alumina, 15 - 30wt% (it calculates as xeransis alumina) binder, 10, - 40wt% ] -- the [ VIb group metal (preferably Mo and/or W), 1, - 10wt% (it calculates as a metallic oxide) ] -- it consists of a VIII group metal (preferably Co and/or nickel)

[0012] With the conventional technique, this zeolite-beta is passing through the two following steps, makes the inclusion proportion of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> increase, and becomes possible [ denaturalizing ]. 1. Step which carries out mosquito glow of several hours zeolite-beta at 500-600 degrees C in order to remove deamination:organic amine mold (template agent) by mosquito glow in elevated temperature. 2. Step which inorganic acid of a certain concentration and zeolite-beta are made to react, and removes aluminum from skeleton of zeolite-beta at specific temperature in order to make inclusion proportion of dealminization-ized:SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> by acid treatment increase.

[0013] After it reduces the acidity of zeolite-beta of a start material to 0.8-1.0mmol/g after making it deaminate by the mosquito glow in an elevated temperature, and processing of an acid performs dealminization-ization after that, the acidity of zeolite-beta is reduced to 0.5-0.6mmol/g. It is not enough for making the selectivity to a middle distillate increase substantially although the amount of the solid acid of the above-mentioned denaturation zeolite-beta can be reduced to some extent.

[0014]

[Embodiments of the Invention] It prepares by carrying out acid treatment of the zeolite-beta for carrying out a mosquito glow of the zeolite-beta of a start material for denaturation zeolite-beta of this invention for deamination, and dealminization-izing, and carrying out hydrothermal processing under the hyperbaric pressure after that. The inclusion proportion of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> of denaturation zeolite-beta concerning this invention can be high, the amount of a solid acid can be reduced, and denaturation zeolite-beta used with the hydrocracking catalyst which starts this invention by doing so can provide a catalyst now with the outstanding selectivity to a middle distillate.

[0015] Zeolite-beta used with the catalyst concerning this invention is the denaturation zeolite prepared according to the process of the above-mentioned this invention. - Since it is beta, and this

gives the high adsorptivity to a non-polar hydrocarbon and only a low adsorptivity is shown in a polar molecule like water, it is usually a hydrophobic zeolite. - It is referred to as beta or denaturation super-hydrophobic-property zeolite-beta. The diameter of the pore of the above-mentioned zeolite-beta used with the catalyst concerning this invention is >5x10-10m. Hydrothermal processing is 400-900 degrees C in temperature after the deamination by the mosquito glow, and dealminization-izing by acid treatment, and under the water vapor pressure of 50-500KPa, and the process feature which prepares the above-mentioned zeolite-beta is a thing made preferably in 0.5 - 5 hours for 0.5 hours of being few.

[0016] Although it is changing the structure of a zeolite in order for the purpose of hydrothermal processing of zeolite-beta currently used by this invention to make the selectivity of the hydrocracking catalyst over a middle distillate increase, hydrothermal processing before dealminization-izing by a mosquito glow or acid treatment under an elevated temperature in the conventional technique of the technique (the purpose of this processing is mainly removing organic amine mold from a zeolite) is another.

[0017] After dealminization-izing, the amount of the acid fraction of zeolite-beta concerning this invention decreases, and the acidity also falls to 0.2-0.3mmol/g preferably 0.1 to 0.5 mmol/g. For this reason, although the requirements in the hydrocracking catalyst cracking activity of this invention for producing the nature fraction of inside are fulfilled, since there is a site with low acidity on the other hand, the possibility of the 2nd cracking decreases. In another side, the grade of dealminization-izing of zeolite-beta of this invention is controlled severely, and the inclusion ratio of SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> in denaturation zeolite-beta obtained here serves as the domain of 30-90.

[0018] Denaturation super-hydrophobic-property zeolite-beta of this invention is a denaturation zeolite which has the degree of bottom-acid nature. It is the denaturation zeolite which has sufficient cracking activity as compared with zeolite-Y although the acidity of denaturation zeolite-beta of this invention is low, therefore is combined with an acid amorphous silica alumina, and becomes one component as shown in Table 1. - The hydrocracking catalyst of this invention which consists of beta shows not only high acidity but the high selectivity to a middle distillate. Furthermore, since comparatively high structure destructive temperature is held, this catalyst is excellent in the thermal stability. Thus, it can use not only the outstanding selectivity [ as opposed to good catalytic activity or a good middle distillate for the above-mentioned zeolite-beta concerning this invention ] but in order to prepare the hydrocracking catalyst which shows a good thermal stability and the resistance over a nitrogen poisoning or a carbon store.

[0019]

[Table 1] (Table 1: Property of zeolite-beta before and behind denaturation)

ゼオライトの型	U S Y	Hゼオライト-β	本発明のゼオライト-β
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> の比率(mol/mol)	6.55	49.16	62.16
酸性度(mmol/g)			
B 酸性	0.634	0.245	0.115
L 酸性	0.301	0.184	0.097
B + L 酸性	0.935	0.429	0.212
構造破壊温度(℃)	1080	1340	1420

An amorphous silica alumina is used for the catalyst concerning this invention as the acidic component and carrier component of an addition of a catalyst. 10 - 60wt%, as for specific surface area, 0.7-1.2ml [ g ] /and acidity are 0.3-0.5mmol/g, an activity carrier component and a zeolite component give cracking activity to union \*\*\*\*\* and a catalyst, and 300-500m<sup>2</sup>/g and pore

volume support [ the content of SiO<sub>2</sub> in this amorphous silica alumina ] the metal component for hydrogenation.

[0020] By the conventional various techniques known well, a pellet product and in order to extrude, to be made to a configuration like a product and to support a metal, the technique of the catalyst concerning this invention, such as coprecipitation, kneading, mixture, and sinking in, is also usable. As for the metal component of the catalyst product concerning this invention, preparing by technique, such as extrusion molding and sinking in, is desirable. Especially the catalyst of this invention, adding the 15 - 30wt% (catalyst all weight criteria) binder prepared by carrying out the peptization of the small pore alumina from an acid like a nitric acid This invention [ 5 - 40wt% of ] (catalyst all weight criteria) denaturation zeolite-beta is mixed to 30 - 80wt% (catalyst all weight criteria) the xeransis powder and homogeneity of an amorphous silica alumina. The mixture is kneaded with a paste. then, generally Extrusion molding is carried out to the bar of the cartridge whose diameter is 1.3-1.8mm, or a special configuration product like a crowbar form. furthermore, after that, a carrier is dried and it activates by the mosquito glow -- making -- the [ at least one periodic-table ] -- the [ VIb group metal and / at least one ] -- the solution containing the hydrogenation metals supported, such as VIII group metal It is prepared from activating in order to make it sink in by the pore saturation or the solution sinking-in method, to dry further the carrier rod with which those metals are supported after that and to acquire the catalyst of this invention.

[0021] The catalyst of this invention is a 10 - 30wt% denaturation zeolite on the basis of the total weight of a catalyst. - beta, A 20 - 40wt% (it calculates as a xeransis alumina) amorphous silica alumina, the [ periodic-table ] -- the [ a 20 chosen from VIb group, - 30wt% (it calculates as a metallic oxide) metal (preferably Mo and/or W), and ] -- a 4 chosen from VIII group, - 8wt% (it calculates as a metallic oxide) metal (preferably) It is desirable that Co and/or nickel are included.

[0022] Although the catalyst of this invention used for hydrocracking is suitable when processing the heavy hydrocarbon raw material which has 250-600 degrees C in the \*\*\*\* domain of 300-550 degrees C especially preferably, it has gas oil, a vacuum distillate, a deasphalted oil, the recycling oil generated from catalyst cracking, \*\*\*\* \*\*\*\*\*, a coal tar, etc. as stock oil which has the special feature described above. Generally, for 100-5000, and space velocity to happen by 0.1-5.0hr-1, and, as for this reaction, reaction temperature is made for the proportion of 5 - 20MPa, hydrogen, and oil to happen [ the bottom of hydrogen presence, and reaction pressure ] at 350-450 degrees C. A hydrocracking process consists of a prior processing phase of the hydrorefining for saturating the polycyclic formula aromatics in stock oil so that relief of the severe operation status in the case of performing the phase and hydrocracking which remove most of S and N from stock oil can be performed. The catalyst of this invention can show comparatively strong resistance to nitrogen, that is, for the reason, a catalyst can be independently used by realizing versatility on use by that cause, and a heavy hydrocarbon raw material can be processed in a single-stage process using a single catalyst. This catalyst shows high selectivity to comparatively high catalytic activity and middle distillate.

[0023] In case the catalyst concerning this invention is used for processing of usual VGO, the bottom of presence of hydrogen and a pressure are [ the reaction ] desirable, and reaction temperature is [ for 500-2000, and space velocity to happen by 0.5-2.0hr-1, and ] made for the proportion of 10 - 20MPa and hydrogen pair oil to happen at 370-420 degrees C. According to hydrocracking, in case the catalyst concerning this invention produces the nature distillate of inside, it has high catalytic activity and the selectivity to a middle distillate. # When it is the same technique as the case of #3812, i.e., the almost same invert ratio, about the catalyst of this invention, reaction temperature is made into 389 degrees C and Daqing VGO is processed for the comparison with 3812 hydrocracking catalyst, the selectivity to a middle distillate is 75w%. It is possible to produce the kerosene for aeronautical navigation and Diesel oil to a production upper limit by being able to use it for operation with the full recycling mode or the single path mode which the versatility on operation use is in the catalyst of this invention, for example, was doubled with the requirements on a product, and regulating an operating

condition. Furthermore, the catalyst of this invention shows the performance which was excellent in hydrocracking and the point of a \*\*\*\*\* low, and the quality of the product which was obtained according to hydrocracking for the reason is excellent. The Diesel oil of a low freezing point can be produced by using the catalyst of this invention especially, the domain of the \*\*\* boundary point of a diesel fraction is wide, and this is convenient to production increase of Diesel oil.

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**EXAMPLE**

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[Example] this invention is explained still in detail with reference to the following example. Instantiation is the purpose and, as for the example explained here, this invention is not limited to these examples.

[0025] [Example 1] H type zeolite-beta ( $\text{SiO}_2 / \text{aluminum}_2\text{O}_3 = 25.1$ ) was processed by 0.5N and HCl for 2 hours, and it carried out hydrothermal processing at 750 degrees C for 2 hours so that water adsorbability in case water vapor pressures are 12mmHgs at 25 degrees C might become 2.6wt% further so that water adsorbability in case the inclusion proportion of  $\text{SiO}_2 / \text{aluminum}_2\text{O}_3$  is [ water vapor pressures ] 12mmHgs at 48 or 25 degrees C might become 16.9wt%. Zeolite of after xeransis and this invention - beta (FA) was obtained. adding the binder (binder) prepared by carrying out the peptization of the pseudo-boehmite which has 28g small pore in the catalyst (CA) of this invention using the dilution nitric-acid solution made to melt 5.7ml of a nitric acid in 85ml distilled water 40% 20.7g zeolite FA, the amorphous silica alumina (the content of  $\text{SiO}_2 -- 45\text{wt}\%$  --) with 86.3g big pore 0.956ml [ g ] /and acidity 0.40mmol/g, [ specific surface area ] [ 365m<sup>2</sup>/g and pore volume ] 47g meta-tongue state ammonium and 42.1g nickel nitrate are mixed uniformly. Knead to a paste the mixed liquor obtained as a result, and a diameter extrudes it through the plate with a hole with 1.7mm cylinder-like pore further. After [ which extruded and dried the rod at 110 degrees C for 3 hours ] obtaining as a result, by making it activate at 500 degrees C A 23.8wt%  $\text{WO}_3$ , a 7.4wt%  $\text{NiO}$ , 10wt% hydrophobic zeolite - It consisted of beta and catalyst CA whose pore volume specific surface area is 264m<sup>2</sup>/g, and is 0.322ml/g was obtained.

[0026] [Example 2] H type zeolite-beta ( $\text{SiO}_2 / \text{aluminum}_2\text{O}_3 = 25.1$ ) so that water adsorbability in case the inclusion proportion of  $\text{SiO}_2 / \text{aluminum}_2\text{O}_3$  is [ water vapor pressures ] 12mmHgs at 48 or 25 degrees C may become 16.9wt% It processes by 0.5N and HCl for 2 hours, hydrothermal processing is carried out at 550 degrees C for 2 hours, and it dries after that so that water adsorbability in case water vapor pressures are 12mmHgs at 25 degrees C may become 7.3wt% further, and it is the zeolite of this invention. - beta (FB) was obtained. the amorphous silica alumina (the content of  $\text{SiO}_2 -- 25\text{wt}\%$  --) with the big pore (41.6g and 116.4g) of the zeolite FB 332m<sup>2</sup>/g and pore volume are mixed in 0.922ml [ g ] /, and acidity mixes [ specific surface area ] 0.34mmol/g uniformly. Then, the binder which was made to carry out the peptization of the pseudo-boehmite with 28g small pore, and prepared it with the dilution nitric-acid solution made to melt 5.7ml 40% nitric acid in 85ml distilled water is added. Furthermore, after that, make mixed liquor knead with a paste and it is extruded through the plate with a hole with the pore of the shape of a cylinder whose diameter is 1.7mm. Dry the extruded rod at 110 degrees C, it was made to activate at 500 degrees C for 3 hours, a 39g molybdenum oxide, 41g nickel nitrate, and the solution prepared from 85% of  $\text{H}_3\text{PO}_4$  were infiltrated, and the carrier was produced. The carrier with which a metal is supported is activated at 500 degrees C after that for 3 hours, and it is a 23.4wt%  $\text{MO}_3$ , 6.7wt%  $\text{NiO}$ , and 15wt% hydrophobic zeolite. - It consisted of beta and the catalyst (CB) of this invention whose pore volume specific surface area is 268m<sup>2</sup>/g, and is 0.329ml/g was acquired.

[0027] the amorphous silica alumina (the content of  $\text{SiO}_2 -- 35\text{wt}\%$  --) of the large pore (62.4g and

106.3g) of zeolite FA obtained in the [example 3] example 1 396m<sup>2</sup>/g and pore volume are mixed in 0.996ml [ g ] /, and acidity mixes [ specific surface area ] 0.34mmol/g uniformly. The binder prepared by carrying out a peptization with the dilution nitric-acid solution which melted 5.7ml of a nitric acid in 85ml distilled water 40% is added. Make the mixed liquor obtained as a result knead with a paste, and it extrudes after that through the hole vacancy plate with the cylinder-like pore whose diameter is 1.7mm. Extrude, dry a rod at 110 degrees C, and the carrier into which the solution which was obtained as a result, and which was prepared by 47g meta-tongue state ammonia and 42.1g nickel nitrate was infiltrated is obtained. Furthermore, it is made to activate at 500 degrees C for 3 hours, and is a 24.5wt% WO<sub>3</sub>, 6.8wt% NiO, and 30wt% hydrophobic zeolite. - It consisted of beta and the catalyst (CC) of this invention whose pore volume specific surface area is 278m<sup>2</sup>/g, and is 0.318ml/g was acquired.

[0028] It prepared by the same technique as an example 1 except having used zeolite Y (acidity being 1.1mmol/g) of a super-hydrophobic property, such as USY which described above the [example 1 of example 4= comparison] contrast catalyst instead of hydrophobic zeolite-beta in this invention. This contrast catalyst consisted of a 22.3wt% MoO<sub>3</sub>, a 7.2wt% NiO, and 15wt% zeolite Y, and the specific surface area is 301m<sup>2</sup>/g, pore volume is 0.386ml/g, and it considered as the contrast catalyst (YC).

[0029] 14.7MPas and hydrogen pair oil proportion used 1200, the pressure used 200ml fixed-bed reactor on condition that 1.5hr-1, and space velocity evaluated the catalyst in the [example 5] examples 1-4. The catalyst was made to sulfurate before evaluation. Table 2 shows the property of the evaluated raw material oil. In the case of the one step in-series process, the 2nd reactor was filled up with the hydrocracking catalyst and the 1st reactor was filled up with the hydrorefining catalyst. Consequently, the nitrogen content of the refining oil included in the 2nd reactor became [g] less than in 10microg /. Table 3 shows the evaluation result of an one step in-series process. Table 4 shows the evaluation result of the one step in-series process of full recycling operation, and shows the property of the processing product in Table 5. Because of the strong resistance over the acidic-site property and nitrogen, the catalyst of this invention is the single-stage process which used the single catalyst, and can process a raw material. Table 6 is as a result of [ at the time of processing Daqing VGO according to the single-stage process which used a single catalyst and contrast catalyst #3812 ] evaluation.

[0030]

[Table 2] (Table 2: Property of raw material oil)

原料オイル	Shngli VGO	Daqing VGO	Saudi Arabian VGO
密度(g/cm <sup>3</sup> )	0.8861	0.8571	0.9133
留出範囲(℃)			
IBP	294	284	319
50%	443	453	432
95%	529	531	504
残留炭素(wt%)	0.15	0.04	0.08
S (wt%)	0.53	0.07	2.20
N (wt%)	1.72	0.54	0.79

[0031]

[Table 3] (Evaluation result of 3:1 steps of tables in-series process uniprocessing)

N.o.	1001	1002	1003
触媒	CA	CB	CC
原料	Saudi VGO	Arabian	Saudi Arabian VGO
		Saudi Arabian VGO	
反応温度(℃)	390	378	375
製品内訳(原料基準vol%)			
ライトナフサ	4.6	5.0	5.6
ヘビーナフサ	10.1	10.1	11.0
航空用灯油	36.1	37.5	38.2
ディーゼル	27.4	26.4	23.5
テール油	30.2	29.2	29.1
液状物收率	108.4	108.2	107.4
中質油選択率(%)	81.2	80.9	78.8

[0032]

[Table 4] (Evaluation result of 4:1 steps of tables in-series process full recycling processing)

N.o.	1004	1005
触媒	CB	YC
原料	Shengli VGO	Shengli VGO
反応温度(℃)	380	384
製品内訳(原料基準vol%)		
ライトナフサ	12.8	23.2
ヘビーナフサ	14.9	16.1
航空用灯油	47.1	44.6
ディーゼル油	33.2	24.0
C <sub>5</sub> .液状物收率	108.0	107.9

[0033]

[Table 5] (Table 5: Property of a hydrocracking product)

N.o.	1001	1002	1003	1004	1005
航空用灯油の発煙点	26	27	28	30	28
ディーゼル油の凍結温度	-11	-14	-17	-12	0

[0034]

[Table 6] (Table 6: It evaluates as a result of a single catalyst and one step process processing)

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